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By

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TOWARD ELECTRICALLY PUMPED ORGANIC DIODE LASERS: ELECTROLUMINESCENCE OF PROTON TRANSFER POLYMERS

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ABSTRACT

Electroluminescence from a series of polymers and copolymers which exhibit photoinduced excited-state intramolecular proton transfer (ESIPT) is reported. Among these polymers containing ESIPT moieties in the main chain or side chain are poly(1,4-(2-hydroxy)phenylene benzobisthiazole-co-decamethylene benzobisthiazole), poly(styrene-co-3-hydroxy-4'-ethenylflavone) and poly(2,5-benzoxazolediyl(2,2,2,-trifluoro-1-(trifluoromethyl) ethylidene)-5,2-benzoxazolediyl-4-hydroxy-1,3-phenylene). The electroluminescence spectra of these polymers are identical to their photoluminescence spectra, indicating that electroluminecence originates from electrically-generated intramolecular proton transfer (EGIPT). Because electroluminescence from EGIPT implies electrically-induced population inversion, these results demonstrate the possibility of electrically-pumped organic solid-state laser diodes.

INTRODUCTION

Photoinduced excited-state intramolecular proton transfer (ESIPT) in heterocyclic aromatic molecules has been widely studied [1]. Molecules exhibiting ESIPT, such as 2-(2-hydroxyphenyl)benzimidazole (HBI) [2], 2-(2-hydroxyphenyl)benzothiazole (HBT) [3], 2-(2-hydroxyphenyl)benzoxazole (HBO) [4], and 2-(2-hydroxyphenyl)benzotriazole (HPB) [5], show a broad and structureless emission with a large Stokes shift that is characteristic of the keto tautomer. In most cases, the fluorescence from the primary excited state (enol form) is quenched due to the very rapid (< 1 ps) photoinduced proton transfer. Molecules exhibiting ESIPT have been used as photostabilizing additives to protect polymers from photochemical degradation [6,7].

The inherent population inversion that ocurs in molecules exhibiting ESIPT was early reconized and proposed as the basis of new laser materials [8]. Proton transfer dye lasers have been demonstrated using salicylamide [9], sodium salicylate [10], and HBI [10] in nonpolar solvents. Optically-pumped solid state dye lasers which show significantly increased lasing efficiency and dye photostability have been realized by covalently attaching HBI derivatives onto poly(methyl methacrylate) (PMMA) chains compared to physical blends of the HBI with PMMA [11].

There is a growing interest in applications of conjugated polymers in optoelectronic devices such as light-emitting diodes [12]. Incorporation of proton transfer moieties into conjugated polymers might lead to new electroluminescent materials with the thermal stability of conjugated polymers and the photochemical stability of proton transfer molecules. Systematic studies on the effects of molecular size, conjugation length, and competition with excimer formation suggested that extended conjugation is the most important factor that can inhibit the proton transfer in such polymers [13,14]. The results also showed that molecular

size does not inhibit ESIPT and that the barrier to ESIPT can be lower than the barrier to excimer formation in polymers exhibiting ESIPT [13,14].

The successful development of semiconducting polymer light emitting diodes (LED) [12] and recent demonstration of optically-pumped lasers [15] in the same class of materials have now focused interest in the prospects of making electrically-pumped laser diodes [15-17]. The question of whether electrical pumping can produce the necessary population inversion in organic semiconductors has become of central importance to this quest. The recent report of electrically-generated intramolecular proton transfer (EGIPT) and stimulated emission from proton transfer polymers has provided the first affirmative answer to this question [17]. In this paper we report investigation of the EGIPT process in several proton transfer polymers with different structures shown in Figure 1. The investigated polymers include poly(1,4-(2-hydroxy)phenylene benzobisthiazole-co-decamethylene benzobisthiazole) (HPBT-co-PBTC10), poly(styrene-co-3-hydroxy-4'-ethenylflavone) (PS-co-V3HF), and poly(2,5-benzoxalediyl(2,2,2-trifluoro-1-(trifluoromethyl)ethylidene)-5,2-benzoxazodiyl-4-hydroxy-1,3-phenylene) (mH6FPBO).
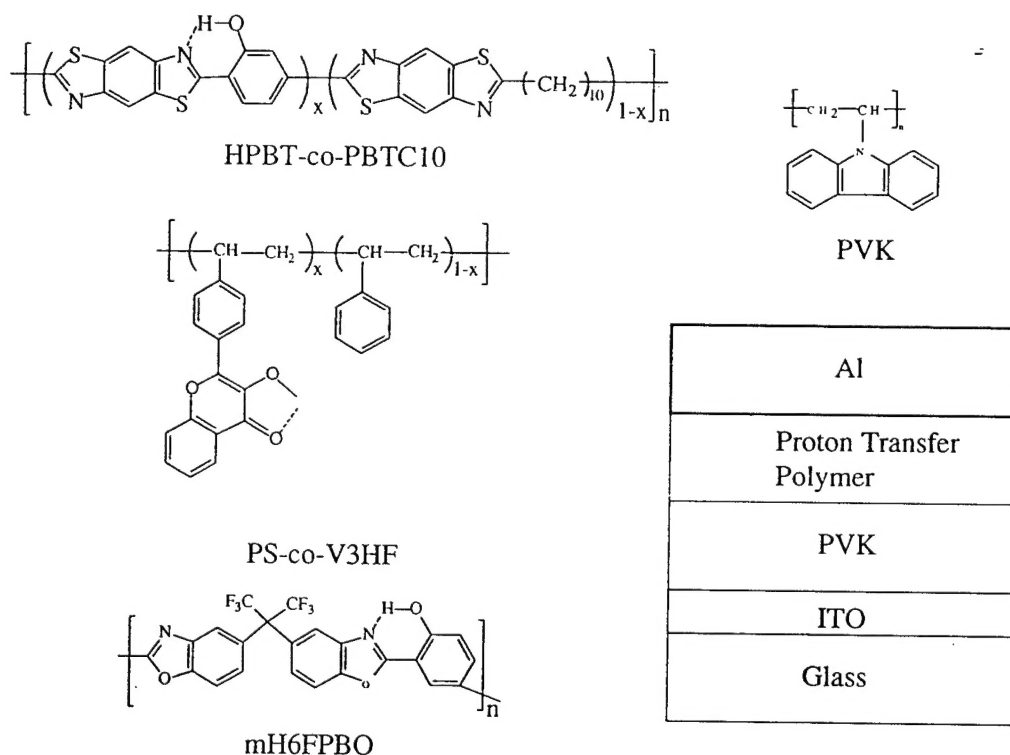

HPBT-co-PBTC10

PVK

PS-co-V3HF

mH6FPBO

Al
Proton Transfer Polymer
PVK
ITO
Glass

Figure 1. Molecular structures of proton transfer polymers and a schematic the LED.

EXPERIMENTS

The synthesis and characterization of the proton transfer polmers shown in Figure 1 have previously been reported [14,17,18]. The structure of the electroluminescence (EL) devices is also shown in Figure 1. First, a layer of 50 nm poly(vinyl carbazole) (PVK) was deposited onto the ITO (indium tin oxide) coated glass substrate by spin coating from dichloroethane solution. The PVK layer functions as the hole transport layer and electron blocking barrier to confine electrons within the emissive layer. Next, a 50 nm layer of a proton

transfer polymer, the emissive layer, was spin coated from formic acid (HPBT-co-PBTC10 and mH6FPBO) or toluene (PS-co-V3HF) solutions. After drying the films in vacuum oven at 80 °C for 12 hours, an aluminum electrode (electron injecting electrode) of 50–100 nm thick was thermally evaporated at high vacuum (below 10^{-5} torr). Optical absorption measurements were done using a Perkin-Elmer Lambda-9 UV/vis/near-IR spectrophotometer. Photoluminescence (PL) and electroluminescence spectra were taken by using a Spex Fluorolog-2 spectrofluorimeter. Current-luminance-voltage curves were recorded simultaneously by hooking up an HP4155A semiconductor parameter analyzer together with a Grasby S370 optometer equipped with a calibrated luminance sensor head. All measurements were performed under ambient conditions.

RESULTS

Figure 2 shows the optical absorption and PL spectra of 5 and 15 % HPTB-co-PBTC10 and the corresponding conjugated homopolymer, poly(1,4-(hydroxy)phenylene benzobisthiazole) (HPBT). The copolymers have an absorption peak at 396 nm whereas the corresponding homopolymer HPBT has an absorption peak at 448 nm. It can be seen that HPBT homopolymer shows only excimer emission [19] with the emission peak at 590 nm. But the emission peak of 540 nm in HPBT-co-PBTC10 copolymers is independent of compositions (x=1–40 %). Therefore, this peak originates from the ESIPT emission [13,14]. The blue shoulder in the PL spectra of HPBT-co-PBTC10 copolymers depends on the rigid-rod segment composition. Below 5%, the intensity of the blue shoulder is negligibly small compared to the ESIPT emission band. In the 10–40 % copolymers, the relative intensity of the blue shoulder to the ESIPT emission band increases with increasing HPBT segment composition. The blue shoulder emission can be assigned to the enol tautomer [13,14].
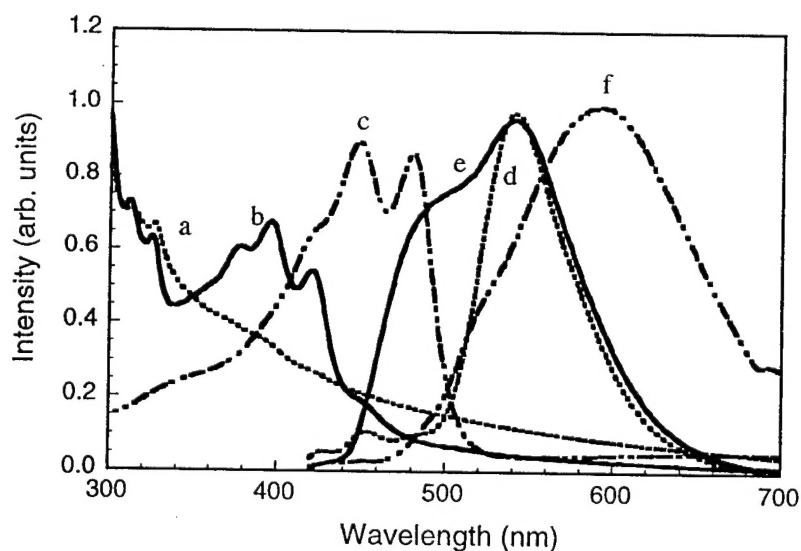

Figure 2. Optical absorption spectra of HPBT-co-PBTC10 copolymer system: (a)5 %, (b)10 % and (c)100 % HPBT. The PL spectra are for 5 % (d), 10 % (e) and 100 % HPBT (f), all with excitation wavelength of 400 nm.
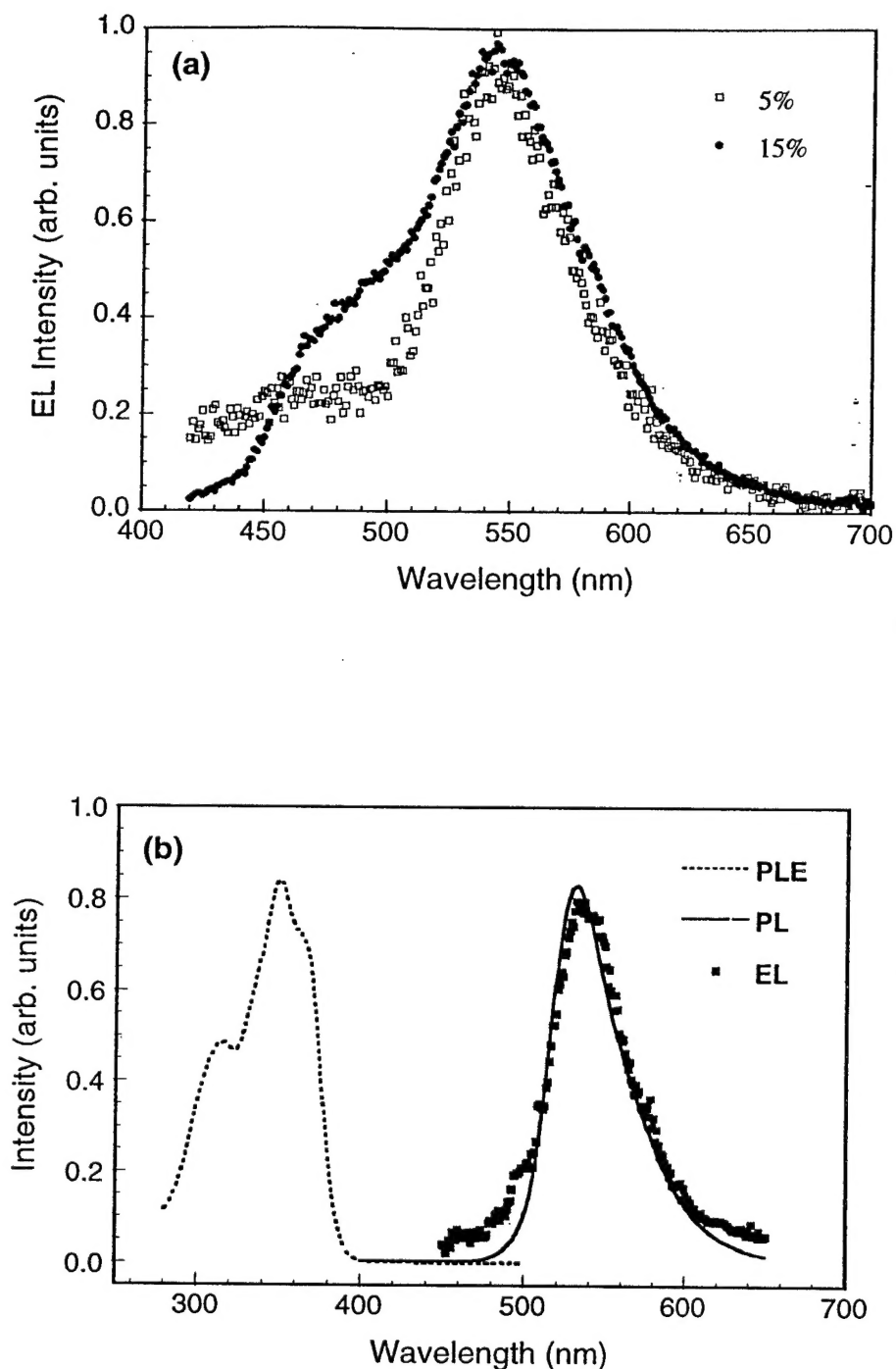
Figure 3. (a) Electroluminescence spectra of 5% and 15% HPBT-co-PBTC10.
(b) PL excitation, PL, and EL spectra of 10% PS-co-V3HF.

All the HPBT-co-PBTC10 copolymers (x=1, 5, 10, 15, and 40 %) exhibited electroluminescence. Figure 3a shows representative EL spectra for the 5 % and 15 % HPBT-co-PBTC10 copolymers. The EL emission peaks in both the 5 % and 15 % copolymers are the same as those in PL spectra (Figure 2). The 5 % HPBT-co-PBTC10 device shows an ESIPT emission band at 540 nm with only a very weak band at ~460 nm. The 15 % copolymer EL device shows a blue shoulder (~475 nm) as well as the 540 nm ESIPT emission band. Figure 3b shows the PL excitation, PL, and EL spectra of the 10 % PS-co-V3HF (The 2% copolymer

showed the same results). An excitation peak at 349 nm was observed whereas both PL and EL spectra have the same peak at 532 nm. Similar results were obtained for mH6FPBO proton transfer polymer which showed an emission peak at 505 nm for both PL and EL. The fact that these proton transfer polymers have identical PL and EL spectra shows that the EL emission of these proton transfer polymers originates from electrically-generated proton transfer (EGIPT) reaction. The excited keto tautomer (K*) formation in the photoinduced ESIPT process is well documented to occur by proton transfer from the primary excited enol tautomer state (E*). However, the detail mechanism of formation of K* by electrical pumping is yet to be elucidated but the overall EGIPT reaction can be expressed by [17]:

$$E^- + E^+ \rightarrow K^* + E \rightarrow E + E + h\nu \tag{1}$$
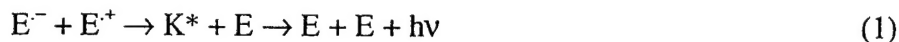
After formation of enol radical anions E^- and radical cations E^+ by electrical injection, it is not clear whether K* forms from E* or from K^- and K^+ recombination. Nevertheless, electrical generation and EL emission from K* which does not exist in the ground state demonstrate electrically induced population inversion in an organic LED. To achieve laser emission by electrical pumping requires that the excitation density be sufficiently large, just as in the case of optical pumping. This means that the concentration of K* produced by EGIPT needs to be much higher than exists in current devices

Figure 4 shows the current-voltage (I-V) and luminance-voltage curves of representative ITO/PVK/15 % HPBT-co-PBTC10/Al device under forward bias (positive polarity at the ITO electrode). It can be seen that the current starts to rise at 10 V and luminance starts at about 13 V. All proton transfer polymers studied here showed similar LED turn-on voltages of 12–13 V. The devices presented here are not optimized yet. The luminance of these devices is relatively low, 2–5 cd/m^2. Clearly, significant improvement in the LED performance will be needed bfore possible laser emission can be expected.
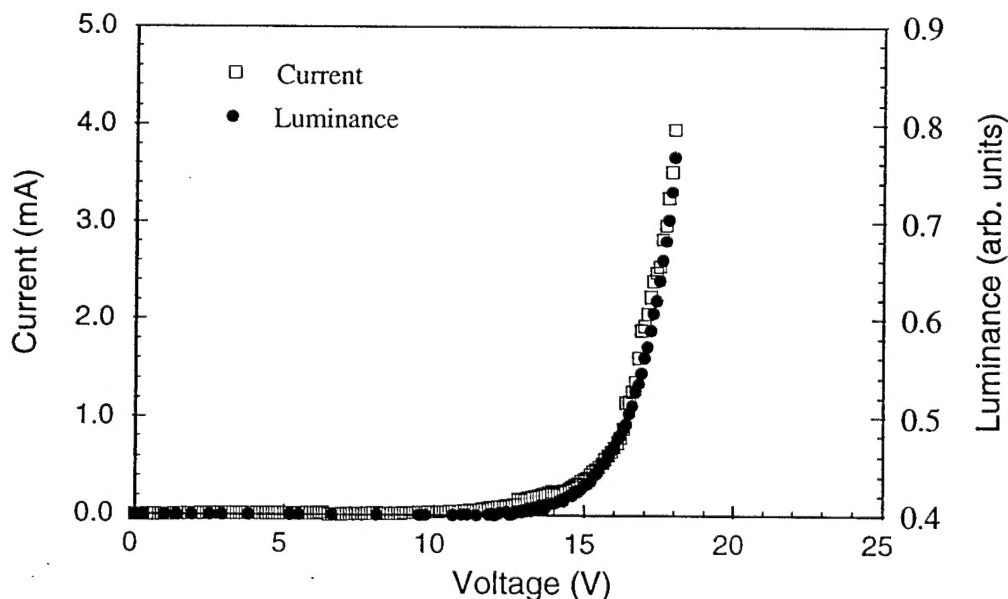

Figure 4. Current-voltage and luminance-voltage curves of the
15% HPBT-co-PBTC10 LED under forward bias.

CONCLUSIONS

Our results demonstrate that proton transfer can occur by current injection into polymers with ESIPT moieties. The electrically generated intramolecular proton transfer process and the resulting electroluminescence demonstrate electrically induced population inversion in an organic LED, a necessary first step toward electrically pumped laser diodes. Together with the prior observation of stimulated emission in the same EGIPT polymers [17], our results suggest that proton transfer polymers exhibiting EGIPT are promising candidates for electrically-pumped organic laser diodes.

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